(19) Europäisches Patentamt
European Patent Office
Office uropéen d s brevets

(11) Publication number: **0 385 053 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 89830082.7

(51) Int. Cl.5: **D06N 1/00, C08L 91/04**

(22) Date of filing: **28.02.89**

(43) Date of publication of application:
05.09.90 Bulletin 90/36

(84) Designated Contracting States:
AT BE CH DE ES FR GB GR LI LU NL SE

(71) Applicant: **MONDO S.p.A.**
Via Arcivescovado, 5
I-10121 Torino(IT)

(72) Inventor: **Stroppiana, Fernando**
Via Alba/Narzole, 7
I-12055 Diano d'Alba (Cuneo)(IT)

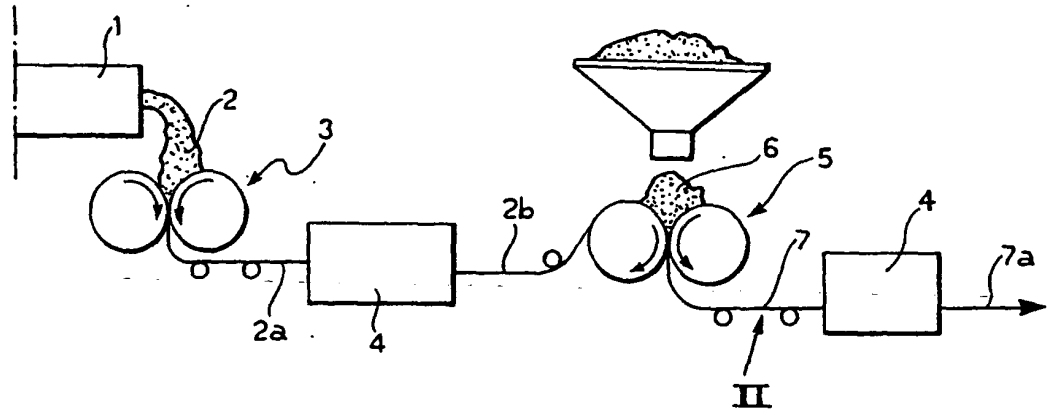
(74) Representative: **Bosotti, Luciano et al**
c/o Jacobacci-Casetta & Perani S.p.A. Via Alfieri, 17
I-10121 Torino(IT)

(54) Method for production of linoleum.

(57) A method for the production of linoleum

A method for the manufacture of a sheet covering (7a) starting from natural oils subjected to oxidation (6) enables the step of seasoning the finished product to be eliminated by virtue of the addition, before the calendering, of cross-linking and accelerating agents which enable the product to be vulcanised rapidly. It is also possible to eliminate the conventional jute fabric by coupling in a calender (5) with a backing sheet (2b) based on a vulcanisable elastomeric material.

FIG. 1



EP 0 385 053 A2

A meth d for the producti n f lin leum

The present invention relates to a method for the production of sheet covering of the linoleum type, including the steps of oxidising a natural oil, adding to the oxidised oil additives selected from the group consisting of colophony, calcium carbonate, cork, wood flour and titanium oxide, and calendering the paste obtained to form a sheet product.

The oxidised natural oil (linoxyn when one starts from linseed oil) has a rubbery consistency and is called "linoleum cement". The cement has additives added to it so as to form a paste which is applied by means of a calender to a backing fabric, normally of jute. The sheet product must subsequently be seasoned by heating for 20 to 30 days in a suitable oven in which the product assumes its final consistency.

The seasoning step predominates over all the other steps for making the product as it requires a long stationary period for the product, to the detriment of the final cost.

Moreover, during heat-seasoning (at about 90° C), the natural oxidation-cross-linking process involves solely the two outer faces of the sheet product, that is, the visible surface and the undersurface where it normally impregnates the jute fabric. In other words, the product is not homogeneous and the removal of the surface film reveals a more malleable paste which is softer and has poorer qualities of wear than the surface.

An object of the present invention is to provide a method of the type specified at the beginning of the description, which enables the disadvantages to be overcome and enables a cheaper linoleum to be produced with better characteristics than the conventional linoleum.

According to the invention, this object is achieved by virtue of the fact that the additives added to the paste obtained from the oxidised natural oil before calendering are cross-linking and accelerating agents, and in that, after calendering, the sheet product is heated for a time sufficient to allow it to vulcanise.

The oxidation-cross-linking of the sheet product is thus "piloted" by the use of cross-linking systems similar to those used in rubber technology.

Examples of the natural starting oils used and subjected to oxidation are linseed oil, fish oil, wood oil, grape-pip oil, hempseed oil, and tomato-seed oil. The steps for the conventional production of linoleum will not be described in detail here since they are well known to experts in the art.

According to the present invention, to the normal additives added to the so-called cement before calendering (mineral fillers, cork, wood, pigments etc.), there is added a suitable mixture of accelerating and cross-linking agents (cross-linking system) adapted to ensure vulcanisation after calendering.

Among the accelerants and cross-linking agents which may be used in the method of the invention are the following inorganic compounds: sulphur chloride, sulphur, zinc, zinc oxide, iron oxide, magnesium oxide, lead oxide, antimony oxide, chromium oxide, calcium oxide.

Among the organic accelerating-cross-linking agents which may be used to advantage are the following: N-cyclohexyl-2-benzothiazylsulphenamide; (N,N′)-diphenyl-guanidine; dibenzothiazyl disulphide; tetramethylthiuram monosulphide; tetraethylthiuram disulphide; N-dicyclohexyl-2-benzothiazylsulphenamide; N,N′-diorthotolylguanidine; N-oxydiethylenbenzothiazylsulphenamide; 2-(4-morpholinyl)-mercaptobenzothiazole; 2-mercaptobenzothiazole; zinc 2-mercaptobenzothiazole; tetramethylthiuram disulphide; zinc dibutyldithiocarbamate; zinc diethyldithiocarbamate; zinc dimethyldithiocarbamate; sodium dibutyldithiocarbamate; sodium dimethyldithiocarbamate; tetrabutylthiuram disulphide; diphenyldiethylthiuram disulphide; 2-mercaptoimidazoline; diethylthiourea; N,N′-diisopropyl-2-benzothiazylsulphenamide; zinc N-ethylphenyl-dithiocarbamate; zinc N′-pentamethylene-dithiocarbamate; 4,4′-dithiodimorpholine; 2-benzothiazolyl-N,N′-diethylthiocarbamylsulphide; N-tert-butyl-2-benzothiazolsulphenamide; N-cyclohexyl-2-benzothiazolsulphenamide; zinc dithiocarbamates; ammonia; amines; thiourea; isocyanates; bis-2-4-dichlorodibenzoylperoxide; N-nitrosodiphenylamine; phthalic anhydride; benzoic acid; stearic acid; organic peroxides such as alkylaralkyl, aralkyl, dialkyl, diaralkyl, diaryl benzoyl, dibenzoyl, 2,4-dichlorodibenzoyl, tertiary dibutyl, dicumyl, tertiary butylcumyl peroxides; condenstation products of acrolein homologs and aromatic bases; tricrotonylidenetetramine; hexamethylene tetramine; cyclohexylethylamine; polyethylenepolyamine; diphenylthiourea; organic salts of lead; dimer of 2,4-toluylendiisocyanate; hydroquinone dioxyethyl ether.

Preferably, th accelerating and cross-linking agents are selected from the group consisting of calcium oxide, active zinc, zinc oxide, stearic acid, sulphur, N-cyclohexyl-2-benzothiazylsulphenamide, tetraethylthiuram disulphide, di-(2,2′-benzo-thiazolyl-) disulphide, tetramethylthiuram monosulphide, (N,N′)-diphenylguanidine and 4,4′ - dithiodimorpholine.

After the calendering of the product, th latter is heated to a high temperature and subjected to a

compression cycle so that, with the vulcanising, it acquires th necessary mechanical characteristics and resistanc to abrasion.

A further object of the present invention is to eliminate the backing fabric, for example, of jute or a synthetic textile (nylon, polyester or the like), to which the paste must be applied to give the product the necessary strength.

The paste obtained cannot in fact be calendered without the aid of the backing fabric and the sheet product without the backing fabric would not have the mechanical properties which would allow the subsequent working steps. One thinks, for example, of the loading of the sheet product into suitable maturing silos where the product is suspended from suitable supporting rolls at a height of several metres from the ground, so as to create a festoon of the sheet with a height of up to 20 metres; without the supporting web the sheet would tear.

As well as the additional cost of the other ingredients of the linoleum, the use of the backing fabric considerably complicates the production and gives the finished product poor flexibility which, for example, makes it more difficult to lay on a floor than rubber coverings.

According to the invention, these disadvantages are eliminated by the fact that the sheet product obtained from the linoleum paste is coupled to a backing sheet of elastomeric material.

The backing sheet is preferably vulcanised after coupling to the sheet product.

The cross-linking reactions which occur in the backing sheet during vulcanisation also involve the region in which the backing sheet itself is joined to the sheet product obtained from the linoleum paste, thus allowing "chemical" bonding between the two component layers of the finished product.

This bonding is particularly strong if the linoleum paste has cross-linking and accelerating agents added to it before calendering, as described above.

Indeed, by coupling a backing sheet based on a vulcanisable elastomeric material to a sheet product obtained from a linoleum paste to which cross-linking and accelerating agents have been added, it is possible to vulcanise the backing sheet and the linoleum layer simultaneously and thus ensure that the coupled product is "monolithic" and has considerable mechanical strength.

A further embodiment of the invention provides for the manufacture of a backing sheet including, as well as vulcanisable elastomeric material, a linoleum paste of conventional type or with cross-linking and accelerating additives. Vulcanisable linoleum paste of the type identical or similar to that subsequently coupled to the backing sheet may be mixed with the vulcanisable elastomeric material up to an amount at which the backing sheet still has sufficient mechanical strength.

As well as eliminating the reinforcing fabric from the linoleum production, the use of the backing sheet ensures the cohesion of the linoleum in a manner similar to that achieved with the fabric of jute or the like and enables the linoleum to be stabilised while minimising the shrinkage of linoleum obtained by to the conventional method.

Moreover, by virtue of the presence of the backing layer of elastomeric material or at least containing a percentage of elastomeric material, one has the advantage of ease of laying on the floor since the product is more flexible.

A further advantage relates to the barrier effect ensured by the backing sheet which prevents moisture in the floor on which the sheet product is laid from damaging the linoleum itself.

The elastomeric material usable as the component of the backing sheet may be selected from natural rubber and synthetic elastomers. All the waste from the working, suitably minced and ground, may to advantage be incorporated in the rubber based backing sheet and possibly in a vulcanisable linoleum paste.

Further characteristics and advantages of the invention will become apparent from the appended examples, which are not to be interpreted in a limiting manner, and from the appended drawings, in which:

- Figure 1 is a diagrammatic view illustrating the method of the invention,
- Figure 2 is a detail of Figure 1 on an enlarged scale,
- Figure 3 is a diagrammatic side view of a continuous heating press used in the method of the invention downstream of the calender,
- Figure 4 is a diagrammatic side view of another type of continuous press usable in the method of the invention, and
- Figure 5 is a diagrammatic view of a hot-air circulating oven usable for vulcanising the sheet product.

With reference to the drawings, an extruder 1 supplies a vulcanisable material 2 to a first calender 3. The vulcanisable material 2 is a mixture of linoleum cement and synthetic or natural elastomeric polymers, as will become clear from th following examples.

At the outlet from the first calender 3, the non-vulcanised backing sheet, indicated 2a, is supplied to a heating press or oven 4. The heating press may be of the type illustrated in Figure 3 or in Figure 4.

With reference to the solution illustrated in Figur 3, the non-vulcanised backing sheet 2a is in contact with a conv yor b lt 12, for example of steel, which passes in a closed loop around a heating drum 14, two counter-rollers 16, and a tensioning roller 18. The drum 14 and the rollers 16 and 18 are supported by a structure 20 and are disposed so as to make the backing sheet 2a follow a circular path in contact with the heating drum 14. The tensioning roller 18 is urged in the direction of the arrow F so as to compress the sheet between the heating drum 14 and the conveyor belt 12. Clearly, the greater the force F applied to the tensioning roller 18, the higher the pressure with which the sheet 2a is kept pressed between the drum 14 and the conveyor belt 12.

In Figure 4, the backing sheet 2a is made to travel a curved path guided by a conveyor belt 22 and a plurality of rollers 24 placed beneath the conveyor belt 22. The latter is housed within a structure 26 in which a temperature suitable for ensuring total or partial vulcanisation of the product is maintained.

The variant of Figure 5 illustrates an oven 4 for vulcanising the sheet 2a without the sheet being squashed. The suitable temperature is maintained by the circulation of hot air by fans 30 and the sheet advances along a sinuous path supported by a plurality of rollers 32.

At the outlet of the heating press or oven 4, the vulcanised or partially-vulcanised backing sheet, indicated 2b, is passed to a second calender 5 which is also supplied simultaneously with a paste 6 of linoleum cement, fillers, cross-linking and accelerating agents. The sheet product 7 leaving the second calender 5 is supplied to a second heating press or oven 4 of the type described above, from which a finished sheet product 7a which is completely cross-linked and ready for use is obtained. The fact that the sheet 7 is not subjected to compression (use of the oven instead of the oven press) has the result of making a final product with a greater porosity than that which can be obtained with the pressers 3 and 4.

When the second calender 5 is supplied with a conventional linoleum paste composed of linoleum cement and fillers, the second heating press or oven 4 may be used to complete the cross-linking of the backing sheet 2b so as to ensure its proper adhesion with the linoleum sheet.

The invention will now be described in greater detail with reference to the following examples, provided by way of non-limiting example, with reference to the various formulations of the product as well as different process conditions. The Examples 1 and 2 which follow relate to a linoleum provided with a fabric backing.

EXAMPLE 1

The following formulations relate to a conventional linoleum cement containing, on average, 60% of linoxyn, 12% of colophony, 24% of calcium carbonate, and 4% of a drying agent.

Various formulations were tested and, with reference to 100 parts by weight of linoleum cement, had the contents given in Table 1 below.

TABLE 1

(formulations)										
	A	B	C	D	E	F	G	H	I	L
Cement	100	100	100	100	100	100	100	100	100	100
Cork	30	65	-	20	20	20	20	20	10	10
Wood flour	66	47	70	50	50	50	50	50	60	60
Titanium dioxide	10	10	20	20	20	20	20	20	20	20
Calcium carbonate	40	40	40	40	40	40	40	40	40	40
Zinc	5	5	5	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1	1	1	1
Calcium oxide	1	1	1	1	1	1	1	1	2	10
N-cyclohexyl-2-benzothiazylsulphenamide (CBS)	2	2	2	2	-	-	1.5	1.5	2	2
Tetraethylthiuram disulphide (TETD)	1	1	1	1	-	-	1.0	1.0	1	1
Sulphur	3	3	3	3	3	3	0.6	0.6	3	3
Dibenzothiazyldisulphide (MBTS)	-	-	-	-	2	2	-	-	-	-
Tetramethylthiuram monosulphide (TMTM)	-	-	-	-	1	1	-	-	-	-
(N,N')-diphenylguanidine (DPG)	-	-	-	-	1	1	-	-	-	-
(4,4')-dithiodimorpholine (DTDM)	-	-	-	-	-	-	1.5	2.0	-	-

EXAMPLE 2

The sheet product obtained according to the formulations D, E, F, G and H in Example 1 were vulcanised with the use of the apparatus illustrated in the drawings. Operational conditions being kept constant, the characteristics of the final product remained almost constant despite the variations in the formulations. Table 2 below shows the variations in the characteristics of the final product with variations in the operational conditions.

TABLE 2

(Operating Conditions)															
Temperature (°C)	110	110	130	130	150	150	110	110	110	110	110	170	200	80	60
Time (minutes)	60	60	30	30	10	10	60	60	60	60	60	5	5	120	240
Pressure (kg/cm^2)	1	-	1	-	1	-	0.5	1.5	2	200	40	1	1	1	1
Punching mm 3.0 (DIN 51855)	0.15	0.50	0.17	0.55	0.18	0.58	O.17	0.15	0.13	0.08	0.10	0.20	0.25	0.14	0.18
Abrasion mm^3	450	600	460	610	480	630	500	450	400	300	350	650	700	445	560
Flexibility (diameter of winding for 3.0 mm sheet) DIN 51849	45	50	45	50	45	55	50	40	40	35	40	55	60	40	50

EP 0 385 053 A2

As may be noted from Table 2, both the punching and abrasion values are better than the average values for a conventional linoleum. Moreover, the stability of shape, breaking strength and elongation of the linoleum obtained according to the method of the invention are also better.

The following example relates to linoleum which does not have a fabric backing since this has been replaced by a backing sheet with an elastomeric matrix, according to the method shown diagrammatically in Figure 1.

EXAMPLE 3

The following formulations of the backing sheet with the elastomeric matrix refer to a linoleum cement given in Example 1.

Various formulations were tested for the backing sheet and it was noted that, although the percentages of linoleum cement and synthetic or natural rubber were varied widely, the backing sheet still had good mechanical characteristics after cross-linking. The most significant formulations for the preparation of the backing sheet are given in Table 3 below, from which it is clear that the cross-linking and accelerating agents are shared by the elastomeric matrix and the linoleum matrix.

TABLE 3

(Formulations used for the production of the elastom ric- and linoleum-based backing sheet)

	A	B	C	D
Linoleum cement	100	5	1	1
SBR (1)	1	25	1	100
Natural rubber	1	25	100	1
Wood flour	80	-	-	-
Calcium carbonate	170	-	-	-
Zinc oxide	8	-	-	-
CBS (2)	3	-	-	-
Eveite (3)	1.2	-	-	-
Sulphur	6	-	-	-
High-styrene resin	10	-	-	-
Kaolin	20	-	-	-
Working waste	20	-	-	-
Stearic acid	2	-	-	-
Coumarone or colophony	2	-	-	-
Calcium oxide	1	-	-	-

(1): styrene-butadiene rubber

(2): sulphenamide - primary accelerant

(3): tetramethylthiuram - secondary accelerant

EXAMPLE 4

With the use of the formulations of Example 3 and the production cycle described above and illustrated in the drawings, and also with the use of the times, temperatures and pressures given in Table 2 above (Example 2), it is possible to obtain a sheet product similar to conventional linoleum without the use of backing fabrics and which is perfectly workable without any problems of tearing of the sheet.

The following example compares the various type of linoleum obtainable by the method of the invention with conventional linoleum matured for more than a year.

EXAMPLE 5

The following types of linoleum were subjected to punching tests at various time intervals A = Linoleum produced by the accelerated cross-linking method of the invention, vulcanised in a press and provided with a jute backing fabric A_1 = Linoleum of type A, also subjected to maturing by oxidation in a conventional oven.

B = Linoleum of type A, without the jute backing but coupled to a rubber backing sheet vulcanised with it in a press.

B_1 = Linoleum of type B, also subjected to maturing by oxidation in a conventional oven.

C = Linoleum produced by the conventional method without cross-linking and without vulcanising, and subjected solely to maturing by oxidation in a conventional oven.

D-E-F = Linoleum products made by the conventional method and matured for more than one year.

The punching data are given in the following table.

TABLE 4

Punching (mm)								
Time / Product	4 hours	1 day	2 days	3 days	4 days	6 days	7 days	14 days
A	0.095	0.085	-	-	0.070	-	0.060	0.065
A_1	-	0.070	0.065	0.050	0.050	-	0.050	0.035
B	0.070	0.060	-	-	0.055	0.050	-	0.06
B_1	-	0.070	0.060	0.050	0.045	0.035	-	0.03
C	pierced	-	-	pierced	-	pierced	pierced	0.25
D	more than one year: 0.070 mm							
E	more than one year: 0.15 "							
F	more than one year: 0.15 "							

As may be seen from Table 4, the linoleum produced according to the invention had characteristics of impressibility comparable with those of conventional products matured for mor than a year.

The values of dimensional stability wer also good, as shown by the following table.

TABLE 5

(dimensional stability)	
Product	
Dimensional variation (DIN 51962)	
Linoleum vulcanised on jute	0.17%
Conventional linoleum on jute	0.15%
Linoleum vulcanised on sheet rubber (without jute)	0.17%

Whenever the backing sheet is coupled to a sheet resulting from a paste linoleum cement and fillers further including cross-linking or accelerating agents, it is possible to obtain the finished product from the vulcanising press after a cycle which may fluctuate between 5 and 10 minutes.

According to a further embodiment of the method, it is possible to mix pieces of linoleum cement with rubbers of the styrene-butadiene type, nitrile rubbers, nitrile-PVC, polybutadiene, EPDM, neoprene and natural rubbers. After this mixing it then suffices to add a cross-linking system to the mixture and to vulcanise the product. Thus it is possible to produce linoleum without the need to make use of a backing of jute fabric or elastomeric sheet material with the resulting advantages both of cost and simplicity of manufacture.

Claims

1. A method for the production of a sheet covering of the linoleum type, including the steps of oxidising a natural oil, adding to the oxidised oil additives selected from the group consisting of colophony, calcium carbonate, cork, wood flour and titanium oxide, and calendering the paste thus obtained to form a sheet product, characterised in that cross-linking and accelerating agents are added to the paste before the calendering and in that, after the calendering, the sheet product is heated for a time sufficient to vulcanise it.

2. A method according to Claim 1, characterised in that the sheet product is heated to a temperature of between 60° and 200° C.

3. A method according to Claim 1, characterised in that, after calendering, the sheet product is subjected to a pressure of between 0.5 and 200 kg/cm^2.

4. A method according to Claim 1, characterised in that the accelerating agents and the cross-linking agents are selected from the group consisting of: calcium oxide, zinc, zinc oxide, stearic acid, sulphur, N-cyclohexyl-2-benzothiazylsulphenamide, tetraethylthiuram disulphide, di-(2,2′-benzo-thiazolyl-) disulphide, tetramethylthiuram monosulphide, (N,N′)-diphenylguanidine, 4,4′ - dithiodimorpholine.

5. A method according to Claim 4, characterised in that the vulcanising time is between 5 and 240 minutes.

6. A method according to Claim 1, characterised in that, before the calendering, the paste is mixed with a vulcanisable rubber.

7. A method for the production of a sheet covering of the linoleum type, including the steps of oxidising a natural oil, adding fillers and additives to the oxidised oil and calendering the paste obtained to form a sheet product, characterised in that the sheet product (6) is coupled to a backing sheet (2b) including an elastomeric material.

8. A method according to Claim 7, characterised in that the backing sheet (2b) is vulcanised after being coupled to the sheet product (6).

9. A method for the production of a sheet covering of the linoleum type, including the steps of oxidising a natural oil, adding to the oxidised oil additives selected from the group consisting of colophony, calcium carbonate, cork, wood flour and titanium oxide, and calendering the paste obtained to form a sheet product, characterised in that cross-linking agents and accelerants are added to the paste before the calendering and in that a backing sheet (2b) including an elastomeric material is coupled to the sheet product (6).

10. A method according to Claim 9, characterised in that, after the backing sheet (2b) has been coupled to the sheet product (6) obtained from the paste, both sheets are heated for a time sufficient to vulcanise them.

11. A method according to Claim 7, characterised in that the backing sheet (2b) is made by calendering

a mixture (2) including, in addition to a vulcanisable elastomeric material, a material resulting from the oxidation of a natural oil together with additives selected from the group consisting of colophony, calcium carbonate, cork, wood flour and titanium oxide, the backing sheet (2b) subsequently being heated for a time sufficient to vulcanise it.

12. A method according to Claim 11, characterised in that the material resulting from the oxidation of a natural oil, used as a component for the manufacture of the backing sheet, has cross-linking agents and accelerating agents added to it.

13. A method for the production of a sheet covering of the linoleum type, characterised in that it includes the following steps:

- supplying to a first calender (3) a mixture (2) including an oxidised natural oil to which there have subsequently been added additives selected from the group consisting of colophony, calcium carbonate, cork, wood flour, titanium oxide, cross-linking agents, accelerating agents, and a vulcanisable elastomeric material,
- heating the sheet material (2a) leaving the first calender for a time sufficient to vulcanise it,
- supplying the sheet (2b) to a second calender (5) which is also supplied with an oxidised natural oil (6) to which there have subsequently been added additives selected from the group consisting of colophony, calcium carbonate, cork, wood flour, titanium oxide, cross-linking agents and accelerating agents, and
- heating the sheet material (7) leaving the second calender (5) for a time sufficient to vulcanise it.

14. A sheet covering of the linoleum type, characterised in that it has a backing layer (2b) including a vulcanised elastomeric material coupled to an upper layer (6) including an oxidised natural oil.

FIG. 1

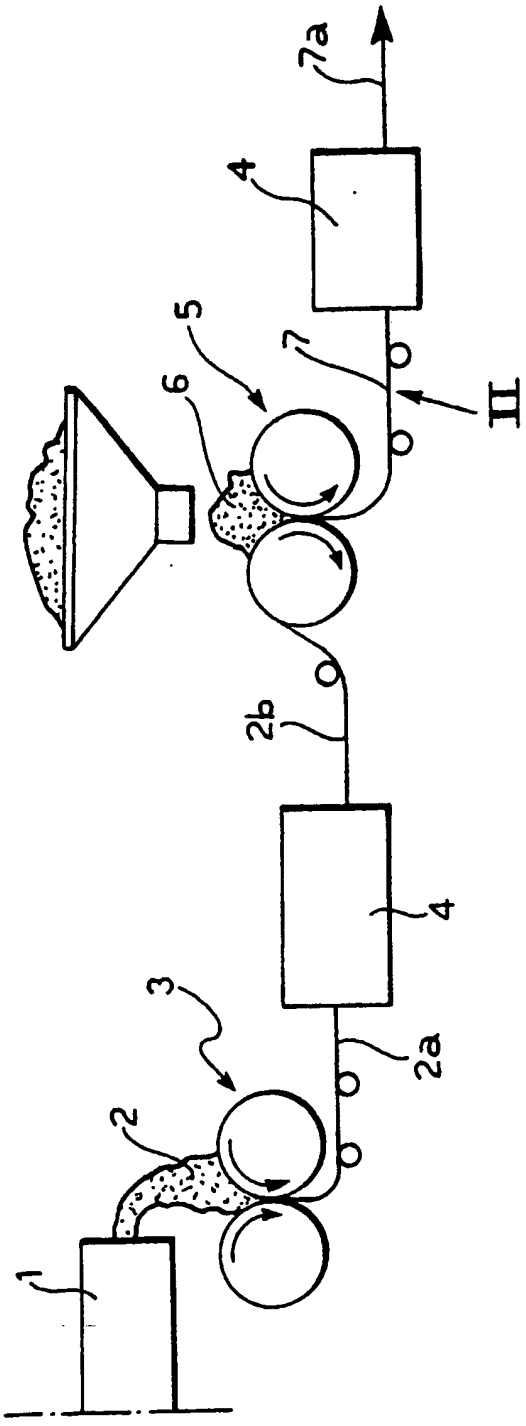


FIG. 2

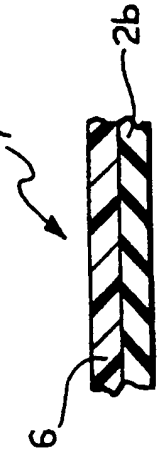


FIG. 3

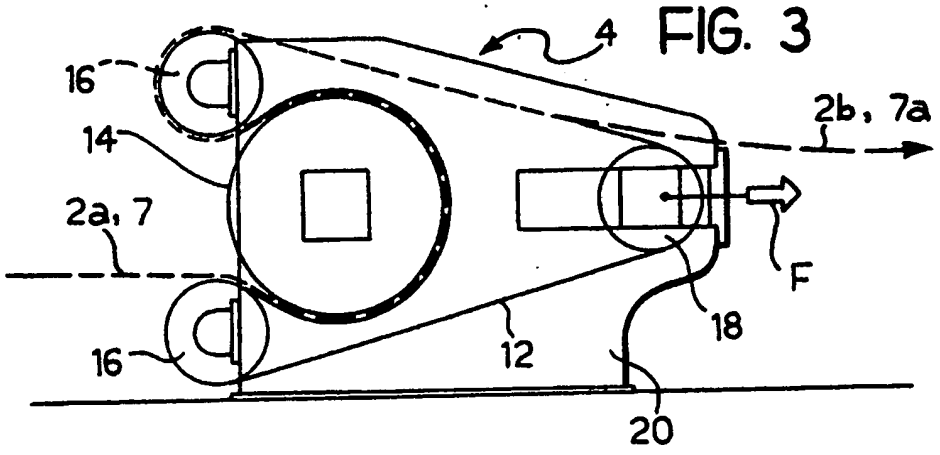


FIG. 4

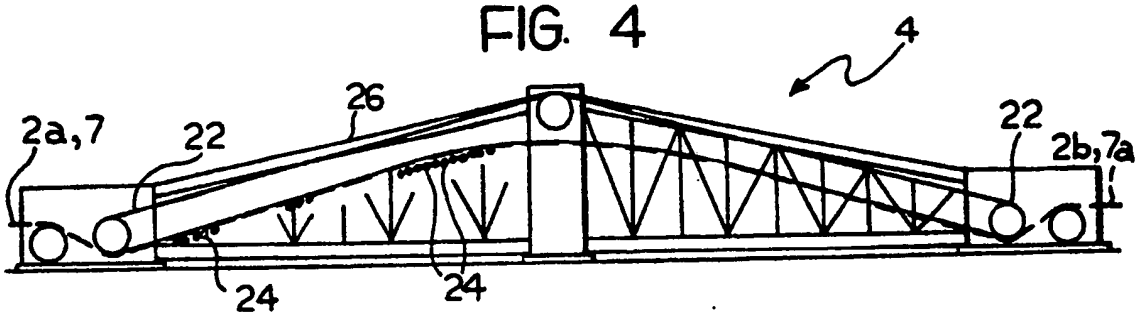


FIG. 5